

# Hydrogen-induced Unzipping of Single-Walled Carbon Nanotubes

Henry Scudder,<sup>1</sup> Gang Lu,<sup>2</sup> and Nicholas Kioussis<sup>1</sup>

<sup>1</sup>*Department of Physics, California State University Northridge, Northridge, CA 91330-8268*

<sup>2</sup>*Department of Physics and Division of Engineering and Applied Science, Harvard University, Cambridge, MA 02138*

The chemisorption of atomic hydrogen on the single-walled armchair carbon nanotube is studied with *ab initio* calculations. A single H atom is found to be chemisorbed on both the inside and outside wall of the nanotube. The binding energy of H adsorption at the exterior of the nanotube is much greater than that at the interior of the nanotube. For the first time, we predict that two rows of H atoms chemisorbed on selective sites *exterior* to the nanotube can break the nearest-neighbor C-C bond of the nanotube through the concerted formation of C-H bonds, leading to the unzipping of the nanotube wall. We provide insights into the underlying electronic structure responsible for the H-induced unzipping of the nanotube, lending strong support to the recent experimental observations for the coalescence of single-walled nanotubes in the presence of atomic hydrogen. Interestingly, H atoms chemisorbed inside the nanotube do not lead to the breaking of the C-C bonds.

Carbon nanotubes have been attracting considerable interest due to their unique electronic and mechanical properties since their discovery about a decade ago [1]. In particular, there have been intense studies in evaluating the capability of carbon nanotubes as hydrogen storage material for clean energy sources [2, 3]. It was found that hydrogen could be stored in bundles of the single-walled nanotubes up to 5-10 wt.% at pressures less than 1 bar near room temperature [4]. The mechanism, for the most part, is attributed to physisorption of H<sub>2</sub> molecules both inside the tubes and within the interstitial regions among the nanotubes at room or low temperatures [4, 5]. However, recently Liu *et al.* observed that, after treating carbon nanotubes with H<sub>2</sub> gas under high pressure, there was residual H<sub>2</sub> during the desorption cycle [3], suggesting the presence of chemisorption in the process. On the other hand, chemisorption can also take place during electrochemical storage processes, in which H<sub>2</sub> molecules are broken into H atoms with the application of metal catalysts or electrochemical techniques [6, 7]. On the theoretical side, first-principles calculations have confirmed the dissociative chemisorption of H<sub>2</sub> on two adjacent nanotubes in solid phase, proceeding with the breaking of the H-H bond concerted with the formation of two C-H bonds on two adjacent nanotubes [8]. The chemisorption of atomic H on single-walled nanotubes has also been observed from self-consistent-charge-density tight-binding calculations [9, 10].

Recently, Nikolaev and coworkers discovered a remarkable phenomenon[11]: under atomic H atmosphere, single-walled armchair nanotubes annealed up to 1500°C coalesce with neighboring tubes, resulting in larger nanotubes with twice and occasionally three times the diameter of the original ones. Based on these observations, the authors proposed a H-activated coalescence mechanism, in which the gas-phase H *atoms* attack the side of neighboring nanotubes, breaking the C-C bonds, and producing defective sites on the adjacent nanotubes. Once these

adjacent defects are formed, the strong thermodynamic force, resulting from the released strain energy in forming larger tubes, drives the two neighboring smaller tubes to join together. Coalescence of clean single-walled nanotubes has also been observed under electron irradiation conditions at elevated temperatures [12].

In this paper, we present a systematic *ab initio* study of chemisorption of H atoms on a single-walled (6,6) armchair carbon nanotube. For the first time, we provide theoretical evidence for the H-induced unzipping of the nanotube. Our theoretical calculations lend strong support to the recent experimental observations of H-activated coalescence of armchair nanotubes [11], revealing the electronic mechanism responsible for this remarkable phenomenon.

The *ab initio* calculations we performed are based on density-functional theory with the CASTEP implementation and ultrasoft pseudopotentials [13]. The Perdew-Burke-Ernzerhof gradient-corrected functional [14] was used for the exchange-correlation potential. The energy cutoff for the plane-wave basis was set to be 300 eV, yielding a convergence for the total energy better than 1 meV/atom. For the reciprocal-space integration we have used eighteen *k*-points along the direction corresponding to the nanotube axis using the Monkhorst-Pack scheme [15]. Results have been obtained for the fully relaxed geometries including all atoms and the lattice constant of the supercell along the tube axis.

The single-walled (6,6) armchair carbon nanotube is modeled with a supercell of dimension 20Å × 20Å × 2.44Å. This corresponds to two layers of C atoms perpendicular to the tube axis with twelve atoms per layer. We have studied three different H coverage, i.e., 1, 2 and 24 H atoms per unit cell. We should point out that due to the periodic boundary conditions along the tube axis, 1, 2 and 24 *rows* of H atoms are actually being simulated in the calculations. The diameter of the fully relaxed pure nanotube is found to be 8.17 Å. The binding energy per

H atom,

$$E_b = 1/n[E_{tot}(tube) + E_{tot}(nH) - E_{tot}(tube + nH)] \quad (1)$$

is calculated in terms of the total energy of the pure nanotube  $E_{tot}(tube)$ , the total energy of the  $n$  ( $=1, 2, 24$ ) H atoms  $E_{tot}(nH)$ , and the total energy of the nanotube with  $nH$  atoms,  $E_{tot}(tube + nH)$ . Since  $E_{tot}(nH)$  is calculated using the same supercell geometry as in the  $(tube + nH)$  system, the spurious adatom-adatom interactions along the tube axis are subtracted. In Table I we list values of the binding energy per H atom at the interior and exterior of the nanotube for one H atom, a pair of H atoms on the same and adjacent layers perpendicular to the nanotube axis, as well as the fully hydrogenated case. The positive value of  $E_b$  in all cases indicates that the chemisorption is exothermic and hence energetically stable.

First, we consider the H coverage of one atom per unit cell, with the H atom adsorbed either at the interior or exterior of the tube. By placing the H atom at various initial positions away from the nanotube wall, we find that there is no energy barrier for H chemisorption at both inside and outside of the tube. Fig. 1(a) shows the relaxed atomic structure with the H atom adsorbed at the exterior to the tube. We label the nearest-neighbor C atom to the H by  $C_1$ , and the nearest-neighbor C atom to  $C_1$  at the same layer by  $C_2$ . The calculated  $C_1$ -H bond length (1.11 Å) is the same for the H atom at either side of the nanotube wall, and it is close to the corresponding value of 1.10 Å in a  $CH_4$  molecule. However, there is a significant difference in the binding energy for H at the interior (0.49 eV) and the exterior (1.77 eV) of the nanotube wall. This is due to the fact that the chemisorption of H results in a transition from  $sp^2$ -like bonding in the pure nanotube to  $sp^3$ -like bonding in the presence of H; and the latter cannot be fully formed upon adsorption to the inner wall because of the unfavorable bonding angle [16]. The Mulliken analysis of bond population [17, 18, 19] shows that 0.33 electrons is transferred from the H atom to its nearest-neighbor  $C_1$ , in agreement with previous calculations [20] for the fully hydrogenated nanotubes. The  $C_1$ -  $s$  and  $p$  orbitals acquire 0.15 and 0.18 electrons, respectively. It is important to note that for the pure nanotube the overlap population between the nearest-neighbor C atoms on the same and two adjacent layers is 0.87 and 2.22, respectively, indicating a stronger bonding in the latter case [18]. This large difference in overlap population between the two types of nearest-neighbor C bonds will in turn affect the propensity of H-induced breaking of the C-C bonds. The chemisorbed H results in an increase of the  $C_1$ - $C_2$  bond length from 1.42 Å (in the pure nanotube) to 1.53 Å, with the latter value being typical for  $sp^3$  C-C bonds. As a result, the  $C_1$ - $C_2$  overlap population decreases from 0.87 to 0.63, indicating that the C-C bond is weakened. In order to gain more insights into

the change of the electronic structure accompanying the H chemisorption process, we have calculated the angular momentum- and site- projected density of states (DOS) for some representative cases (Fig. 2). For the pure nanotube, we have confirmed the metallic behavior of the (6,6) armchair nanotube with a low density of states at the Fermi energy ( $E_F$ ) [1]. From Fig. 2(a), we find that the H chemisorption induces the opening of a band gap ( $\approx 5$  eV) for the  $C_1$  atom, which is the result of the large charge transfer from the H atom to  $C_1$ , filling up the  $C_1$   $p$  valence band. On the other hand, it is interesting to note that the  $C_2$  atom exhibits a large narrow peak across  $E_F$  which overlaps with the bonding states of the H atom. This peak, reminiscent of a Van Hove singularity, arises from the degeneracy of the two linear bands crossing  $E_F$  in the pure nanotube, which is in turn lifted under the local distortion induced by H, thus forming two sub-bands whose extremes fall at  $E_F$ . Fig. 3(a) shows the valence charge density contour plot for a plane containing the C atoms on the same layer. One can see the directional  $sp^2$ -like covalent bonding between the C atoms, the  $sp^3$ -like bonding between  $C_1$  and H, and the weakening of the  $C_1$ - $C_2$   $sp^2$  bond.

The result of the H-induced weakening of the C-C bond invites an interesting question: Could the chemisorption of another H atom on the nearby C atom lead to the formation of two H-C bonds which will in turn further decrease or even break the  $C_1$ - $C_2$  bond, resulting in the unzipping of the entire nanotube? Thus, next we consider the case of a pair of H atoms chemisorbed on the  $C_1$  and  $C_2$  atoms in the exterior and interior to the tube. We have examined two different adsorption sites for the second H atom, either at the same or the adjacent C layer. First, we present results with the interatomic axis between the H atoms parallel to the  $C_1$ - $C_2$  bond. The binding energy per H for this case is 0.37 eV (inside the tube) and 3.0 eV (outside the tube), respectively. As in the single H case, the pair of H atoms prefers to be chemisorbed at the exterior of the nanotube. Interestingly, the binding energy per H atom for the pair outside the nanotube has dramatically increased compared the corresponding value for the single H case, while the charge transfer from each H to its nearest-neighbor C remains about the same (0.30 electrons) as in the one H case. This charge transfer leads to an ionic-like repulsion between the H atoms and between  $C_1$  and  $C_2$ . Figure 1(b) shows the relaxed atomic structure for the case of two H atoms adsorbed at the exterior of the tube on the same layer. The most remarkable feature in this figure is the *breaking* of the nearest-neighbor  $C_1$ - $C_2$  bond. The equilibrium H-C,  $C_1$ - $C_2$ , and H-H bond lengths are 1.09 Å, 4.07 Å, and 2.94 Å, respectively. Due to the periodic boundary conditions along the tube axis, the result implies scission of the nanotube wall along the tube axis, i.e., the unzipping effect necessary for the experimentally observed coalescence phenomenon. The overlap popula-

tion of C<sub>2</sub>-H is 0.71, which is as large as that for the nearest-neighbor C-C bond at the same layer in the pure nanotube. Fig. 2(b) shows the DOS for one of the hydrogenated C atoms, C<sub>2</sub> (see also Fig. 1b) and its nearest-neighbor, C<sub>3</sub>. The DOS for C<sub>2</sub> is similar to that of C<sub>1</sub> in Fig. 2(a). Note the narrowing of the H *s* band which exhibits bonding and antibonding states separated by an energy gap of about 5 eV, indicates that the H atom is stabilized due to the hybridization between the *s* states of H and the *p* states from the nearby C<sub>2</sub> atom. From Fig. 3(b), one can see the *sp*<sup>3</sup>-like bonding between the C and the H atoms, and the breaking of the C<sub>1</sub>-C<sub>2</sub> bond.

We have also studied the case of two H atoms chemisorbed on the two nearest-neighbor C atoms located at adjacent layers shown in Fig. 1(c). The binding energy per H atom is found to be 0.73 eV in the interior and 2.52 eV in the exterior of the tube, respectively. In contrast to the previous case, we find that the nearest-neighbor C-C bond does not break. The equilibrium H-C, C<sub>2</sub>-C<sub>3</sub>, and H-H bond lengths are 1.10 Å, 1.50 Å, and 2.29 Å, respectively. There is a similar amount of charge transfer from the H atoms to each nearest-neighbor C atoms with an overlap population of 0.74. However, in contrast to the previous case, the C<sub>2</sub>-C<sub>3</sub> overlap population of 1.59 is reduced considerably relative to that of 2.2 in the pure nanotube. By employing a larger supercell (four layers per cell), we find essentially the same results, i.e., the C-C bond remains unbroken in the presence of H atoms. This result can be understood from the fact that the nearest-neighbor C-C bonds on adjacent layers are stronger than those on the same layer, as alluded earlier.

Interestingly, the C-C bond can not break when the two H atoms chemisorb inside the nanotube regardless of the adsorption site. The C-C bond deforms nevertheless, with the bond length increasing from 1.42 Å (pure tube) to 1.52 Å. This again originates from the reduced propensity for *sp*<sup>3</sup> bonding at the interior of the nanotube [16]. Overall, the internal surface of the nanotube is found to be less reactive than the external surface, in agreement with the general consensus [21, 22]. Finally, our calculations for the fully endo- and exo-hydrogenated nanotube find no breaking of the C-C bonds and a lower binding energy per H atom of 0.30 eV and 0.84 eV, respectively. We have also carried out calculations for a H<sub>2</sub> molecule approaching the nanotube wall, both from the exterior and the interior, with the H-H bond perpendicular to the nanotube wall. In agreement with previous calculations [8], we find that no chemisorption occurs and the H<sub>2</sub> molecule remains intact.

In conclusion, we have studied the chemisorption properties of atomic H on a single-walled (6,6) armchair nanotube. We find that H atoms bind strongly to the nanotube through *sp*<sup>3</sup> bonding, with the binding energy at the exterior of the tube being much greater than that at the interior. For the first time, we predict that a pair of H atoms chemisorbed on two nearest-neighbor C atoms

on the same layer outside the nanotube catalyzes the breaking of the C-C bond and leads to the unzipping of the nanotube. This H-induced unzipping mechanism lends strong support to the recent experimental observations for the coalescence of single-walled nanotubes in the presence of atomic H. On the other hand, the C-C bond does not break when H atoms are adsorbed at the interior of the tube.

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- [1] M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic, San Diego, 1996); R. Saito, G. Dresselhaus, and M. S. Dresselhaus, *Physical Properties of Carbon Nanotubes* (Imperial College Press, London, 1998).
  - [2] P. Chen, X. Wu, J. Lin, and K. I. Tan, *Science* **285**, 91 (1999).
  - [3] C. Liu, Y. Y. Fan, M. Liu, H. Liu, H. T. Cong, H. M. Cheng, and M. S. Dresselhaus, *Science* **286**, 1127 (1999).
  - [4] A. C. Dillon, K. M. Jones, T. A. Bekkedahl, C. H. Kiang, D. S. B. Bethune, and M. J. Heben, *Nature (London)* **386**, 377 (1997).
  - [5] Y. Ye, C. C. Ahn, C. Witham, B. Fultz, J. Liu, A. G. Rinzler, C. Colbert, K. A. Smith, and R. E. Smalley, *Appl. Phys. Lett.* **74**, 2307 (1999).
  - [6] R. E. Haufler *et al*, *J. Phys. Chem.* **94**, 8634 (1990).
  - [7] L. Becker, T. P. Evans, and J. L. Bada, *J. Org. Chem.* **58**, 7630 (1993).
  - [8] Siu-Pang Chan, G. Chen, X.G. Gong, and Z.F. Liu, *Phys. Rev. Lett.* **87**, 205502 (2001).
  - [9] S. M. Lee and Y.H. Lee, *Appl. Phys. Lett.* **76**, 2877 (2000).
  - [10] S. M. Lee, K. S. Park, Y. C. Choi, Y. S. Park, J. M. Bok, D. J. Bae, K. S. Nahm, Y. G. Choi, S. C. Yu, N. Kim, T. Frauenheim, and Y. H. Lee, *Synth. Met.* **113**, 209 (2000).
  - [11] P. Nikolaev, A. Thess, A. G. Rinzler, D. T. Colbert, and R. Smalley, *Chem. Phys. Lett.* **266**, 422 (1997).
  - [12] M. Terrones, H. Terrones, F. Banhart, J.-C. Charlier, and P. M. Ajayan, *Science* **288**, 1226(2000).
  - [13] D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).
  - [14] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
  - [15] H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
  - [16] K. Tada, S. Furuya, and K. Watanabe, *Phys. Rev. B* **63**, 155405 (2001).
  - [17] R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).
  - [18] D. Sanchez-Portal, E. Artacho, and J. M. Soler, *J. Phys. Condens. Matter* **8**, 3859 (1996).
  - [19] M. D. Segall, C. J. Pickard, R. Shah, and M. C. Payne, *Mol. Phys.*, **89**, 571 (1996).
  - [20] T. Yildirim, O. Gülseren, and S. Ciraci, *Phys. Rev. B* **64**, 075404 (2001).
  - [21] R. C. Haddon *et al*, *Nature* **350**, 320 (1991).
  - [22] S. Park, D. Srivastava, and K. Cho, *Nanotechnology* **12**, 245 (2001).



FIG. 1: Relaxed atomic structures for chemisorption of one H atom (a), and a pair of H atoms on the same layer (b) and on the adjacent layers (c) of the (6,6) single-walled armchair nanotube.

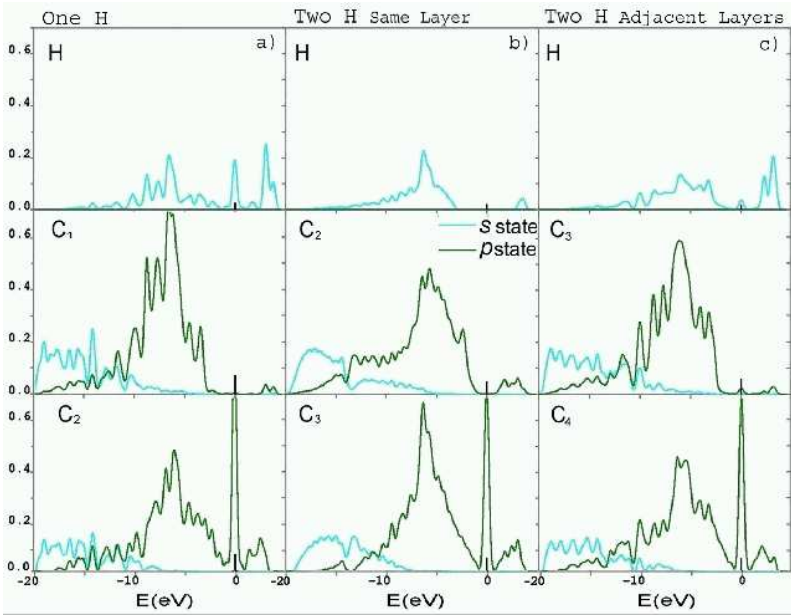


FIG. 2: The angular momentum and site projected DOS for the adsorption of one H atom (a), and a pair of H atoms on the same layer (b) and on the adjacent layers (c), exterior to the nanotube. The labeling of the various atoms is the same as that used in Figs. 1 (a), (b) and (c), respectively.

TABLE I: Binding energy (eV) per H atom for chemisorption exterior and interior to the nanotube for one H atom, a pair of H atoms on the same and the adjacent layers, as well as the fully hydrogenated case.

	1 H	2 H same layer	2 H adjacent layers	24 H
interior	0.49	0.37	0.73	0.30
exterior	1.77	3.00	2.52	0.84

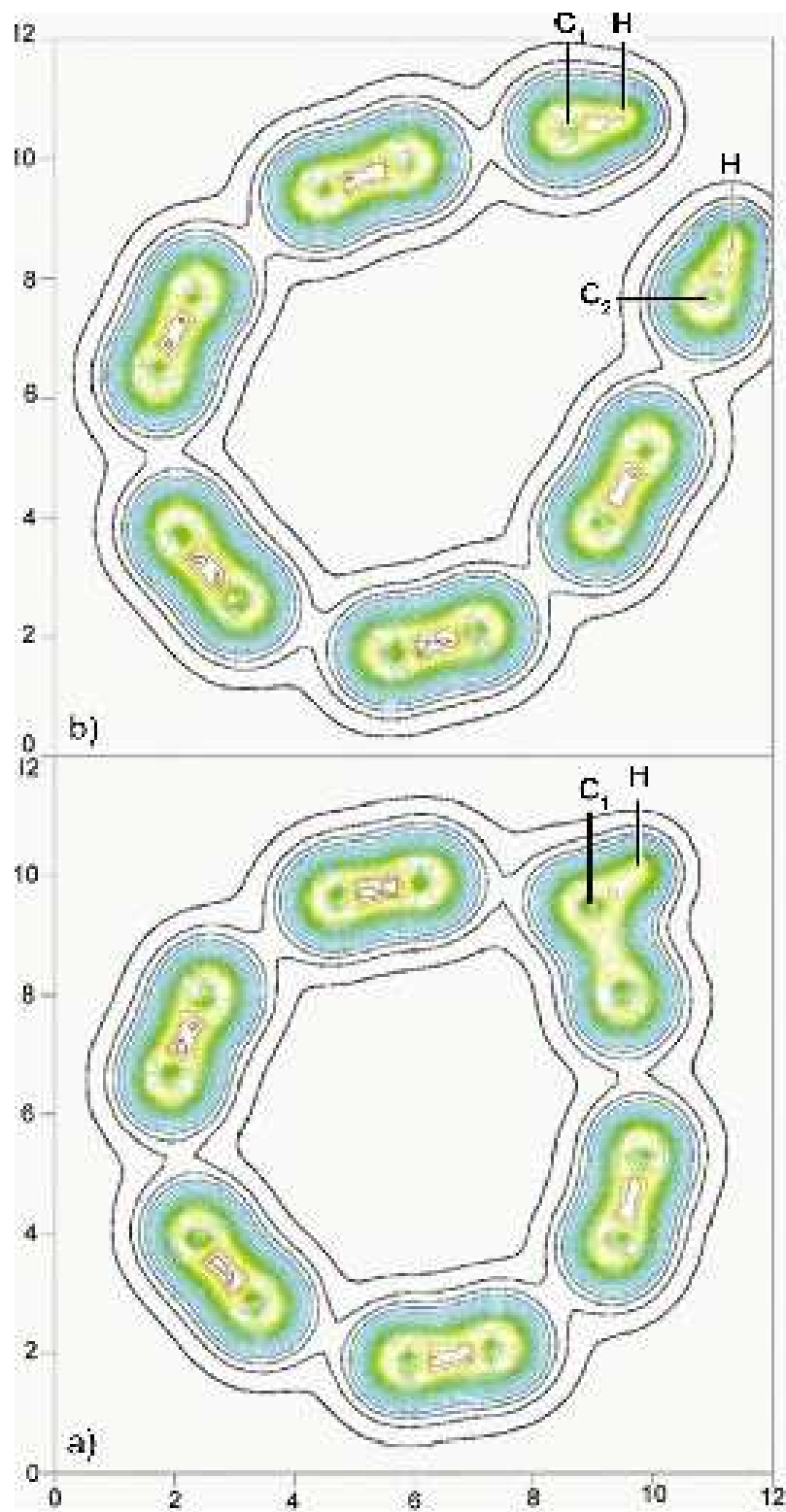


FIG. 3: The valence charge density contour plot on a plane perpendicular to the nanotube axis passing through the C atoms, for adsorption of one H atom (a), and two H atoms on the same layer (b).